

PATENT COOPERATION TREATY

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NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Assistant Commissioner for Patents
 United States Patent and Trademark
 Office
 Box PCT
 Washington, D.C. 20231
 ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 31 March 2000 (31.03.00)	
International application No. PCT/EP99/05329	Applicant's or agent's file reference 95.0108
International filing date (day/month/year) 16 July 1999 (16.07.99)	Priority date (day/month/year) 30 July 1998 (30.07.98)
Applicant BALLARD, David et al	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:

28 February 2000 (28.02.00)

☐ in a notice effecting later election filed with the International Bureau on:2. The election ☒ was☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	Authorized officer Claudio Borton Telephone No.: (41-22) 338.83.38
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INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference 95.0108	FOR FURTHER ACTION see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. PCT/EP 99/ 05329	International filing date (day/month/year) 16/07/1999	(Earliest) Priority Date (day/month/year) 30/07/1998
Applicant SOFITECH N.V. et. al.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.



It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.



the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :



contained in the international application in written form.



filed together with the international application in computer readable form.



furnished subsequently to this Authority in written form.



furnished subsequently to this Authority in computer readable form.



the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.



the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,



the text is approved as submitted by the applicant.



the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,



the text is approved as submitted by the applicant.



the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.



as suggested by the applicant.



because the applicant failed to suggest a figure.



because this figure better characterizes the invention.



None of the figures.

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference WO 55.0186	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/EP99/05329	International filing date (day/month/year) 16/07/1999	Priority date (day/month/year) 30/07/1998
International Patent Classification (IPC) or national classification and IPC C09K7/00		
Applicant SOFITECH N.V. et. al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.



2. This REPORT consists of a total of 6 sheets, including this cover sheet.

- ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 2 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☒ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand 28/02/2000	Date of completion of this report 06. 09. 00
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer olde Scheper, B Telephone No. +49 89 2399 2141 

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/EP99/05329

I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

Description, pages:

1-10 as originally filed

Claims, No.:

1-8 as received on 31/07/2000 with letter of 27/07/2000

Drawings, sheets:

1/2,2/2 as originally filed

2. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/EP99/05329

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	5,7,8
	No:	Claims	1-4,6
Inventive step (IS)	Yes:	Claims	5,7,8
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-8
	No:	Claims	

2. Citations and explanations

see separate sheet

VI. Certain documents cited

1. Certain published documents (Rule 70.10)

and / or

2. Non-written disclosures (Rule 70.9)

see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/EP99/05329

Re Item V

Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Reference is made to the following documents:

- D1: US-A-4 498 540 (M.L.MARROCCO) 12 February 1985 (1985-02-12)
- D2: WO 86 00330 A (CITIES SERVICE OIL AND GAS CORPORATION) 16 January 1986 (1986-01-16)
- D3: GB-A-2 017 124 (KRAUSE MILLING COMPANY) 3 October 1979 (1979-10-03)
- D4: US-A-4 098 997 (M.M.TESSLER) 4 July 1978 (1978-07-04) cited in the application
- D5: EP 0920874 A

The document D6 was not cited in the international search report.

1. The present application relates to a wellbore fluid (claims 1-6), an application (claim 6) or process (claims 7-8) in which said fluid is used.
2. D1 discloses wellbore fluids (column 5, lines 19-36; column 7, lines 5-9; column 7, line 36 to column 8, line 13; column 9, line 47 to column 10, line 34), which appear to differ from those of the present application in that the average molecular weight of the polyvinyl alcohol copolymer is at least 100,000 (column 6, lines 56-60). The gels are formed by acidic catalysis (column 3, line 56 to column 5, line 18). It is to be noted that the particulate materials of the present application swell in water as well and form gel particles.
The gels exhibit improved resistance to heat and are stable in hard water (column 10, lines 9-20). D1 is silent with respect to the removal of gels.
3. D2 relates also to the same technical field as the present application (page 1, lines 1-18). Disclosed are gels obtained by crosslinking polyalcohol with aldehydes (chemically crosslinked structures, i.e. a particle), their application in wellbore fluids, recovering oil, and which are stable under alkaline conditions. It is disclosed that the first substance (for instance polyvinyl alcohol) has a molecular

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weight of at least about 30,000 (page 5, line 7 to page 6, line 16; page 7, line 40 to page 8, line 29; page 9, lines 9-33; page 10, line 10 to page 12, line 4; page 13, lines 1-4; page 15, lines 18-33; claims 47-49, 79-80, 82-84, 86, 89-94, 120, 125-130, 133-134, 136-137, 139-140, 143, 145, 156).

It may be observed that the products are obtained at pH values of between 2 and 5 (page 10, lines 26-28), meaning that the products must be stable under these conditions. It is disclosed at page 15, lines 28-34 that deposits in the well are removed by acid after forming the gel. This also means that the gels are meant to be stable under acidic conditions.

4. The subject-matter of present claims 1-4 and 6 lacks novelty in view of D2 (Art. 33(3) PCT.

It is to be observed that present independent claim 1 is a claim to a product per se. It is characterized by the fact that a particulate material is composed of the reaction product of A and B, which component A exhibits a molecular weight of less than 30,000 and that said particulate material is "water-non soluble".

Products obtained from A and B are known from D2. Gels are products which are water-non soluble. The disclosed value of "at least 30,000" overlaps with the claimed range "less than 30,000". It should be noted that compound having a molecular weight of 29999 might be less than 30000, but is still considered to be anticipated by a product having a MW of 30000.

4. D3 (see examples 9 and 11; page 1, lines 5-27; page 2, lines 3-34) relates to a particulate material composed of the reaction product of A and B, which component A exhibits a molecular weight of less than 30,000.
5. D4 discloses particulate materials based upon oxidized starches and more specific "thin-boiling starches" (see column 2, lines 36-41). It is believed that thin-boiling starches may have molecular weights of about 1000 and higher, also well within the claimed range of 30000 (see D5, paragraphs [0004] and [0007]).
6. It appears that present claims 5, 7 and 8 are not anticipated by the cited prior art. However, novelty and inventive step can only be conclusively established and/or

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acknowledged in the present case if the subject matter of the claims is clear (see Item VIII below).

7. It may be observed that the inventive concept of the present application (formation of a gel of A and B as defined, which can easily be removed by lowering the pH) is not disclosed in the available prior. However, claims 1-4 and 6 are defined in such broad terms that no distinguishing features in view of D2 can be established.

Re Item VI

Certain documents cited

GB-A-2 322 865 (SOFITECH) 9 September 1998 (1998-09-09)

Disclosed are crosslinking agents for polymer solutions for fracturing, remedial and other operations within a wellbore.

Re Item VIII

Certain observations on the international application

1. Present claim 7 is unclear in that it is not specified where this specific process step fits in the various processes defined in claim 6 (Art. 6 PCT).
2. Present claim 7 is unclear in that features like "...of this invention" should not be used in a claim. Further, the present application is not directed to any particulate material, but to a wellbore fluid.
3. Present claim 8 is unclear (Art. 6 PCT) in that it is unclear how starting a flow causes a drop in pH (under all circumstances, in all kinds of well processes).

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Wellbore Fluid

This invention relates to wellbore fluids suitable for use in oil and gas exploration and production industries and embraces fluids used for drilling, under-reaming, completion, cementing, fracturing, stimulation, workover and packing of wellbores and also includes spacer fluids whose function is to separate two fluids during pumping operations and spotting fluids whose function is to treat certain intervals of the wellbore.

In the process of rotary drilling a well, a drilling fluid or mud is being circulated down the rotating drill pipe, through the bit, and up the annular space between the pipe and the formation or steel casing, to the surface. The drilling fluid performs different functions such as removal of drilled cuttings from the bottom of the hole to the surface, suspension of cuttings and weighting material when circulation is interrupted, control of subsurface pressures, maintaining the integrity of the wellbore until the well section is cased and cemented, isolate the fluids from the formation by providing sufficient filtration control to prevent excessive loss of fluids to the formation, cool and lubricate the drill string and bit, maximise penetration rate etc.

The required functions can be achieved by a wide range of fluids composed of various combination of solids, liquids and gases and classified according to the constitution of the continuous phase mainly in two groupings : aqueous (water-based) drilling fluids, and non-aqueous (mineral oil or synthetic-base) drilling fluids, commonly 'oil-base fluids'

Other types of fluid used in well operations include completion fluids, a term which commonly refers to fluids pumped after drilling finishes but prior to starting production, and workover fluids, used in remedial operations usually on a well that is already producing.

During the operations for drilling and completing hydrocarbon-bearing formations (reservoirs), an overbalance pressure is often applied which causes fluid loss from the wellbore into the reservoir rock. This filtration process causes solid particles to block pores in the formation with the build-up of a low permeability internal filtercake comprised of the solid phases present in the fluid as shown figure 1. The depth of invasion may be from a few millimetres to (occasionally) many centimeters. This is the primary cause of damage (loss of productivity) in open hole wells, a phenomenon which is increased by a large overbalance pressure. Furthermore the formation of a thick filter cake may

lead to an increased risk of getting drill pipes or measuring tools stuck in the wellbore and to failure in cementing the wellbore casings.

Mud solid invasion is also important when the well comprises large natural fractures as shown figure 2. The fractures invaded by the mud are no longer available to drain the oil into the wellbore.

5 In workover operations, perforations may be also invaded in the same way.

It is therefore highly desirable to provide means to at least minimise formation damage.

High fluid loss, especially spurt loss, tends to increase mud invasion. Accordingly, additives of a polymeric type such as biopolymers (Xanthan, Scleroglucan), starches and celluloses (hydroxyethyl cellulose[HEC], polyanionic cellulose [PAC]) - are added to provide viscosity and fluid loss control.

10 Usually wellbore fluids also contain inorganic solids such as clays, barite and calcium carbonate. When considering minimising mud invasion, an important aspect in selecting such inorganic solids is their particle size distribution for the particles to seal the entrance to pores or fractures in the reservoir rock. The "bridging" solids are combined with water soluble or colloidal polymers to enhance the seal.

15 Sized particles limit the depth of invasion as shown figure 3 and 4 where the pore or fracture entrance is sealed with bridging solids. The solids used include for instance ground silica (especially common in fracturing operations), mica, calcium carbonate, ground salts and oil soluble resins.

Another often interrelated approach is to use soluble solids to allow subsequent clean-up with wash fluids. Accordingly sized calcium carbonate (that can be dissolved by acid and therefore be removed from the pores) is a typical component of drill-in fluids. The polymers used in conjunction with the calcium carbonate are often selected on the basis that they can also be broken down by acid or enzyme treatments to prevent them impairing the permeability of the formation.

20 However, these remedial treatments involving the use of strong acid (for instance 15% HCl) have a high cost and can be indeed hazardous and ineffective for the following reasons. Poor dissolution of the filter cake can be caused by zones of higher permeability channelling acid away and into the formation. This can lead to further formation damage. Strong acids involve health and safety issues and cause corrosion of sand screens and downhole equipment. Treating a wellbore interval also raises placement issues. Moreover, laboratory tests have shown that the acids can be damaging to the reservoir rock matrix.

Because of these limitations there are many systems and products on the market to try and improve the performance of filter cake clean up treatments. However, these to have associated problems. For example, the use of alkaline oxidising agents can lead to problems of iron oxide scale in metal tubulars. Enzymes take a long time to react and are limited in application by temperature, pH, and salinity. Internal breakers, such as magnesium peroxide, can be added to the reservoir drill-in fluid so it forms part of the filter cake. This is then activated by acid to produce hydrogen peroxide to facilitate the breakdown the polymers in the cake. Unfortunately, this can actually happen in the reservoir drill in fluid whilst drilling which can have a negative effect on fluid properties.

The present invention aims at providing new wellbore fluids which can form an easy-to-remove filter cake.

The invention provides a fluid system that, when used for the purposes of drilling, completing, cementing, stimulating, packing or working over a wellbore, will facilitate filter cake removal. These can be aqueous or non-aqueous based fluids (such as hydrocarbon based fluids). The result will be reduced or often negligible impairment of permeability of the producing formation by the relevant reservoir servicing fluid compared with well servicing fluids containing conventional bridging materials.

In accordance with the present invention, acetal crosslinked polymers are used as the bridging agent in the relevant fluid. In essence the bridging material is made of a particulate material which may swell but is substantially insoluble in water under non-acidic conditions (at pH >7.5) and which is degraded at acidic pH (below 6.5) to substantially solids-free or soluble decomposition products. The particles are composed of the reaction product of A) one or more water soluble organic compound having possessing a molecular weight of less than 30,000 and possessing at least two hydroxyl groups and B) any other organic compound(s) capable of forming acetal or hemiacetal cross-links with the hydroxyl groups of compound A.

Examples of compounds A with free hydroxyl groups capable of entering into the crosslink reaction of the invention include monosaccharides, oligosaccharides, polysaccharides of molecular weight less than 30,000, glycerol, polyglycerols, erythritol, pentaerythritol, mannitol, sorbitol, glycols, polyalkylene glycols, and low molecular weight water soluble vinyl polymers possessing hydroxyl groups.

Suitable acetal crosslink agents B include aliphatic monoaldehydes and dialdehydes having from 2 to 10 carbon atoms and esters of propiolic acid wherein the alcohol forming the ester has from 1 to 8 carbons. A preferred compound is 1,5 pentanedial (glutaric dialdehyde) $C_5H_8O_2$.

Usually, the amount of cross-linking agent varies from 0.5 to 15% w/w (and the amount of compound A accordingly varies from 99.5 to 85% w/w).

An example of a useful material has been prepared from 95% yellow dextrin (a gum produced from the acid hydrolisis and depolymerisation of starch feedstock) and 5% by weight pentanedial.

Acetal crosslinked starches are known from U.S. Patents 4,048,435 and 4,098,997 that describe methods of preparing reversibly crosslinked granular starches for use in the paper, adhesives and textile industries but with no mention as to their potential use in the oil industry. It is stated that these starches contain acetal crosslinkages, which are stable under neutral or alkaline conditions but which readily hydrolyse under acidic conditions, and they are designed to dissolve and form a colloidal suspension in water. By contrast, the present invention contemplates the cross-linking of much lower molecular weight polyols than the above mentioned starches to produce a particulate suspension where the particles do not dissolve or disperse at alkaline pH.

The solid may be ground or prepared to any desired particle size.

The particles are stable under alkaline conditions and insoluble (but usually swell) in aqueous wellbore fluids of pH 7.5 and above. Thus they provide very effective sealing of the formation by virtue of the swollen particles' ability to deform to "fit" the pore openings or fractures.

Most advantageously however, the cross links rapidly hydrolyse under acidic catalysed conditions, under even weakly acidic conditions at pH 6.5 and below. The degradation products are essentially solids free water soluble moieties of low molecular weight and low viscosity in solution. Hence any flow restriction (of hydrocarbons) caused by the particles may be efficiently removed. A low pH solution such as a weak easily-handled acid of little corrosion potential may be pumped in place to catalytically degrade the particles. Alternatively, produced fluids, be they oil and water or gas and water, usually exhibit an aqueous pH of less than pH 6.5 due to the carbon dioxide commonly present. Hence the removal of the temporary seal may be triggered simply by allowing the well to flow. As the seal degrades the well flow increases autocatalytically.

The hydrolysis does not consume the acid. Hence much enhanced clean up and optimised well productivity is anticipated compared to that exhibited when using current materials such as ground calcium carbonate.

The following features and benefits have been identified with the use of acetal crosslinked, polymeric, bridging solids:

- Filter cakes made from these novel materials almost totally degrade in the presence of weak acid giving almost 4x the return flow rate compared to a corresponding calcium carbonate based fluid under the same conditions. This also gives the benefits of better health and security from handling weak acids and less corrosion of downhole screens and equipment.
- A feature of the invention is that the degradation of the acetal bridging material is acid catalysed, as opposed to the conventional stoichiometric reaction. This means the acid is not consumed or neutralised in the reaction. The benefit of this is an enhanced acid treatment as the acid is available to go on degrading more filter cake.
- Due to the high mobility of the hydrogen ion, (which can therefore penetrate the water-swollen particles) the acid does not have to be forced into the filter cake to break it down. Which means that less acid induced damage results from strong acid being forced into the formation causing fines to migrate, bridge and restrict production.
- Acetal crosslinked bridging materials can degrade under simulated well flowing conditions in the laboratory, where the weak acid is provided by produced CO₂ forming carbonic acid in the aqueous phase. This could negate the need for a costly wash fluid treatment.
- Acetal bridging materials have a low density. A low density will enable a wider range of applications to be covered, density constraints often limit the amount of bridging solid which can be used. Calcium carbonate has a density of 2.7 S.G. and cannot always be added at the desired concentrations for bridging in low density fluids. Another benefit will be improved removal of undesirable, non acidisable, contaminating solids, from the fluid. Contaminating solids from the formation have roughly the same density as calcium carbonate which makes separation difficult in a conventional fluid. However, these solids are approximately 2.7 times denser than the acetal bridging solid. This means that highly efficient separation techniques, such as centrifugation, can be employed to remove non acidisable solids from the fluid without removing the acetal bridging solids. This therefore makes the fluid less formation damaging.

Preparation of an acetal bridging solid.

95 weight parts of dry yellow dextrin was dissolved in water and 5 weight parts pentanediol added. The sample was mixed and heated to 130°C. The water was then removed under partial vacuum
5 over a 16 hour period. The solid from this was then ground to a fine particle size (substantially all less than 150 microns) and tested as follows.

The wellbore fluids in the following examples have been tested using a high pressure/high temperature fluid loss cell as schematically represented figure 5. Such an apparatus typically
10 comprises a measuring cell 1 closed by an upper cover provided with a central passage 2 and a bottom provided with a drain 3. The bottom is covered with a base made of a porous material, in this instance a 5 micron aloxite disc. Gas can be injected to provide the differential pressure between the mud and the formation fluids. The product doses are expressed in pounds per barrel (ppb).

15 Example 1

A fluid system of this invention (Acetal fluid) was compared to one of conventional formulation, CaCO₃ based fluid (comparison fluid) containing 49ppb calcium carbonate bridging solids, 6ppb DUALFLO filtration control additive, 1ppb IDVIS viscosifier and suspending agent, 25ppb CaCl₂, 2ppb PTS200 alkaline buffer.

20 The Acetal fluid contains - 40ppb ACETAL bridging solids, 6ppb DUALFLO, 1ppb IDVIS, 43ppb KCl, 2ppb PTS200.

The testing of the fluids was according to the following protocol, schematically illustrated figure 5 where the arrows indicate the direction of the fluid flow in the core plugs (the upwards arrow
25 corresponds to fluid loss from the subterranean rock to the wellbore while the downwards arrow characterises fluid loss from the wellbore into the subterranean rock).

- Step 1: 'apply' mud damage, using the tested wellbore fluid, to a 5 micron aloxite disc under typical well conditions (temperature 80° C, pressure of 500 psi). Fluid loss is measured after 15.5 hours (downwards arrow). A filter cake is formed on the aloxite disc.
- Step 2: cell emptied hot and refilled with 10% NaCl brine and 12/20 sand. A 45 micron aperture screen was then placed on the sand. The sand is used for modelling a gravel pack which may be placed in a well to control sand production.
- Step 3: simulates the flow from the reservoir oil into the wellbore through the filter cake (upwards arrow) , using kerosene flow back and a typical formation pressure of 4 psi with carbon dioxide as the pressuring gas at 80°C.
- Step 4 : Flow 500g of CO₂ containing kerosene, shut the cell and leave for 64 hours at 80°C and then test the flow rate in the production direction

Sample	15.5 hr. Fluid loss	Flow rate after shut in
	(ml)	(g/min)
CaCO ₃ bridging solids	17	22..2
Acetal bridging solids	20	33.6

The example illustrates the effect that an ACETAL fluid filter cake is degraded in the presence of kerosene containing dissolved carbon dioxide. The return flow rate for the ACETAL fluid was 1.5 x higher than for the CaCO₃ fluid. This test suggests that naturally occurring fluids from a production zone will degrade the filter cake even in the absence of applied acid. It can also be seen that using all acetal bridging solids gives a slightly higher fluid loss. It was found that the use of a small amount of calcium carbonate in conjunction with the acetal solids reduced the filtrate loss, allowing a lower concentration of DUALFLO fluid loss additive to be utilised in the following examples.

Example 2

The CaCO_3 based fluid contains - 40ppb calcium carbonate, 6ppb DUALFLO, 1ppb IDVIS, 43ppb KCl, 1ppb PTS100.

The ACETAL based fluid contains - 7ppb calcium carbonate, 30ppb ACETAL solids, 3ppb DUALFLO, 1ppb IDVIS, 43ppb KCl, 3ppb PTS100.

The following test protocol is used

- Step 1: 'apply' mud damage, using the tested wellbore fluid, through a 5 micron aloxite disc at a temperature of 80° C and a pressure of 500 psi. The fluid loss is measured after 15.5 hours.
- Step 2: cell emptied hot and refilled with 100 ml 5% citric acid as a moderated acidic wash fluid.
- Step 3: Reseal cell, do not pressurise, leave 72 hours at 80°C
- Step 4 : Open cell and fill with 12-20 sand and fit 45 micron aperture screen
- Step 5: Carry out kerosene return flows at 4psi, at a temperature of 80°C.

Sample	16.5 hr. Fluid loss (ml)	Flow rate (g/min)	pH of produced fluids
CaCO_3 fluid	23	21.2	5.9
ACETAL fluid	17	80.9	2.0

The example signifies that under mild acid conditions the return flow rate for the ACETAL fluid was nearly 4x higher than for the CaCO_3 fluid, indicating that the ACETAL fluid filter cake has degraded to a much greater extent. This was confirmed on opening the cell which showed the presence of a large filter cake for the CaCO_3 fluid and little to no filter cake for the ACETAL fluid.

The lower pH of the produced fluids from the cell containing the ACETAL filter cake indicates that the acid is not being used up to the same extent as with CaCO_3 filter cake. The example also

demonstrates that the filter cake is degraded without pressurisation of the cell. Conventionally, these tests are typically carried out under pressure to force acid into the cake.

Example 3

- 5 The CaCO_3 based fluid contains - 40ppb calcium carbonate, 6ppb DUALFLO, 1ppb IDVIS, 43ppb KCl, 2ppb PTS200, 15ppb OCMA clay.

The ACETAL based fluid contains - 7ppb calcium carbonate, 30ppb ACETAL solids, 3ppb DUALFLO, 1ppb IDVIS, 43ppb KCl, 3ppb PTS100 15ppb OCMA clay.

- 10 The test protocol of example 2 was used except that step 1 lasted only 15.5 hours and step 3 20hours.

Sample	15.5 hr. Fluid loss	Flow rate
	(ml)	(g/min)
CaCO_3 fluid	32	9.8
ACETAL fluid	18.8	21.4

- 15 The example demonstrates that an ACETAL fluid filter cake containing non acidisable OCMA clay is degraded by weak acid in a short time. The return flow rate for the ACETAL fluid was 2.2 x higher than for the CaCO_3 fluid, indicating that the ACETAL fluid filter cake has degraded to a much greater extent.

Example 4

- 20 The CaCO_3 based fluid contains - 40ppb calcium carbonate, 6ppb DUALFLO, 1ppb IDVIS, 43ppb KCl, 2ppb PTS200.

The ACETAL based fluid contains - 10ppb calcium carbonate, 30ppb ACETAL solids, 3ppb DUALFLO, 1ppb IDVIS, 43ppb KCl, 2ppb PTS200.

The following test protocol was used :

- 5 • Step 1: 'apply' mud damage, using the tested wellbore fluid, through a 5 micron aloxite disc at a temperature of 80° C and a pressure of 500 psi. The fluid loss is measured after 15.5 hours.
- Step 2: cell emptied hot and refilled with 0.1m (0.37%w/v) HCl and 12/20 sand and a 45 micron aperture screen fitted.
- Step 3: The cell was resealed and left for 4hours @ 80°C
- 10 • Step 4: then kerosene flow backs carried out at 4psi and 80°C.

Sample	15.5 hr. Fluid loss (ml)	Flow rate (g/min)
CaCO ₃ fluid	29	20.7
ACETAL fluid	16	32.0

- The example demonstrates that exposure of ACETAL fluid filter cake to even a highly diluted acid causes it to degrade in only a short time. The return flow rate for the ACETAL fluid was 1.5 x
- 15 higher than for the CaCO₃ fluid.

Claims

1. A wellbore fluid comprising a particulate material composed of the reaction product of A) one or more water soluble organic compound having possessing a molecular weight of less than 30,000 and possessing at least two hydroxyl groups and B) any other organic compound(s) capable of forming acetal or hemiacetal cross-links with the hydroxyl groups of compound A.
5
2. The wellbore fluid of claim 1 wherein hydroxyl compound (A) is selected from the class including monosaccharides, oligosaccharides, polysaccharides of molecular weight less than 30,000, glycerol, polyglycerols, erythritol, pentaerythritol, mannitol, sorbitol, glycols, polyalkylene glycols, and low molecular weight water soluble vinyl polymers possessing
10 hydroxyl groups.
3. The wellbore fluid according to claim 1 or 2, wherein compound (B) is selected from the class including aliphatic aldehydes and dialdehydes having from 2 to 10 carbon atoms, and esters of propionic acid wherein the alcohol forming the ester has from 1 to 8 carbon atoms.
4. The wellbore fluid according to any of the preceding claim, wherein 0.5-15%, dry weight of
15 compound (A) and 95.5-85% of said compound (B) is reacted.
5. The wellbore fluid according to any of the preceding claim wherein the particulate material is the reaction product of dextrin and pentanediol.
6. Application of the wellbore fluid according to any of the preceding claim as any of the following well processes : drilling, under-reaming, completing, working over, sealing loss zones, sealing
20 fractures, sealing cavities or other very high permeability conduits in a rock formation, or hydraulic fracturing to stimulate a hydrocarbon-producing zone
7. A process wherein after any of the well processes of claim 6, a low pH fluid containing any acid or buffered solution of less than pH 6.0 is pumped into the producing zone segment of the wellbore to catalyse the decomposition of the particulate material of this invention.
- 25 8. A process wherein, after any of the well processes in Claims 6 or 7, the well is allowed to flow causing a drop in pH which catalyses the decomposition of the particulate solids of this invention permitting yet increased flow of produced fluids.

9. A particulate material composed of the reaction product of A) one or more water soluble organic compound having possessing a molecular weight of less than 30,000 and possessing at least two hydroxyl groups and B) any other organic compound(s) capable of forming acetal or hemiacetal cross-links with the hydroxyl groups of compound A.
- 5 10. The particulate material of claim 9, wherein the hydroxyl compound (A) is selected from the class including monosaccharides, oligosaccharides, polysaccharides of molecular weight less than 30,000, glycerol, polyglycerols, erythritol, pentaerythritol, mannitol, sorbitol, glycols, polyalkylene glycols, and low molecular weight water soluble vinyl polymers possessing hydroxyl groups.
- 10 11. The particulate material as in Claim 9 wherein the compound (B) is selected from the class including aliphatic aldehydes and dialdehydes having from 2 to 10 carbon atoms, and esters of propiolic acid wherein the alcohol forming the ester has from 1 to 8 carbon atoms.

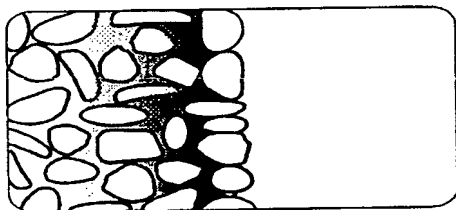


Figure 1

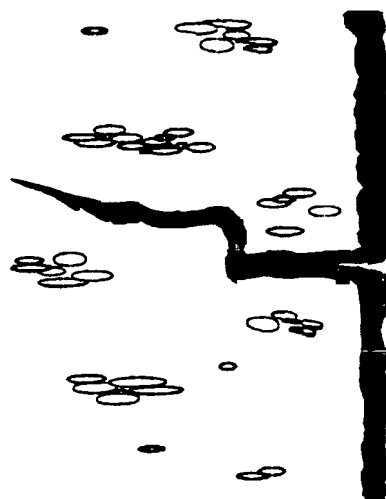


Figure 2

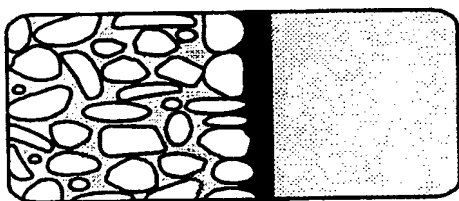


Figure 3



Figure 4

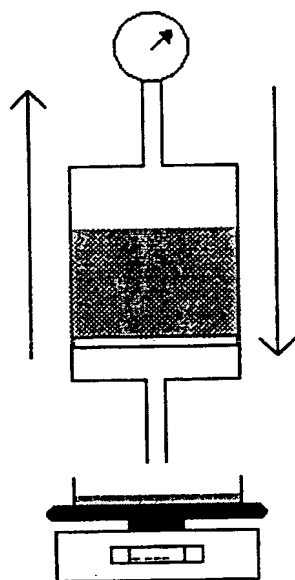


Figure 5

INTERNATIONAL SEARCH REPORT

Application No

PCT/EP 99/05329

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09K7/00 E21B33/138 C07C45/71 C07C47/19 C08B37/00
C08G4/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09K E21B C07C C08B C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4 498 540 A (M.L.MARROCCO) 12 February 1985 (1985-02-12) column 7, line 5 - line 9 column 7, line 36 -column 8, line 13 column 9, line 47 -column 10, line 34 ---	1-3,6,7
Y,P	GB 2 322 865 A (SOFITECH) 9 September 1998 (1998-09-09) page 1, line 4 - line 35 page 7, line 16 - line 29 ---	1-3,6,7
Y	WO 86 00330 A (CITIES SERVICE OIL AND GAS CORPORATION) 16 January 1986 (1986-01-16) page 5, line 7 -page 6, line 16 page 7, line 40 -page 8, line 29 page 9, line 9 - line 33 page 10, line 10 - line 32 page 15, line 18 - line 33 ---	1-3,6,7
-/--		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

17 December 1999

Date of mailing of the international search report

14/01/2000

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INTERNATIONAL SEARCH REPORT

Application No.

PCT/EP 99/05329

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 2 017 124 A (KRAUSE MILLING COMPANY) 3 October 1979 (1979-10-03) page 2, line 3 - line 34; examples 9,11 page 1, line 5 - line 27 ---	9-11
X	US 4 098 997 A (M.M.TESSLER) 4 July 1978 (1978-07-04) cited in the application the whole document -----	9-11

INTERNATIONAL SEARCH REPORT

Information on patent family members

Application No

PCT/EP 99/05329

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
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GB 2322865	A	09-09-1998	NONE	
WO 8600330	A	16-01-1986	AT 122708 T CA 1258734 A DE 3588019 D EP 0186663 A GB 2145420 A,B NO 178903 B US 4643255 A CA 1245388 A CA 1267747 A US 4673038 A CA 1282526 A US 4665986 A CA 1254337 A US 4796700 A CA 1244584 A US 4665987 A	15-06-1995 22-08-1989 22-06-1995 09-07-1986 27-03-1985 18-03-1996 17-02-1987 22-11-1988 10-04-1990 16-06-1987 02-04-1991 19-05-1987 16-05-1989 10-01-1989 08-11-1988 19-05-1987
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WELLBORE FLUID

This invention relates to wellbore fluids suitable for use in the oil and gas exploration and production industries and embraces fluids used for drilling, under-reaming, completion, cementing, fracturing, stimulation, workover and packing of wellbores and also includes spacer fluids whose function is to separate two fluids during pumping operations and spotting fluids whose function is to treat certain intervals of the wellbore.

In the process of rotary drilling a well, a drilling fluid or mud is being circulated down the rotating drill pipe, through the bit, and up the annular space between the pipe and the formation or steel casing, to the surface. The drilling fluid performs several different functions, such as removal of drilled cuttings from the bottom of the hole to the surface, suspension of cuttings and weighting material when circulation is interrupted, control of subsurface pressures, maintaining the integrity of the wellbore until the well section is cased and cemented, isolating the fluids from the formation by providing sufficient filtration control to prevent excessive loss of fluids to the formation, cooling and lubricating the drill string and bit, maximising penetration rate etc.

The required functions can be achieved by a wide range of fluids composed of various combination of solids, liquids and gases and classified according to the constitution of the continuous phase mainly in two groupings : aqueous (water-based) drilling fluids, and non-aqueous (mineral oil or synthetic-base) drilling fluids, commonly 'oil-base fluids'

Other types of fluid used in well operations include completion fluids, a term which commonly refers to fluids pumped after drilling finishes but prior to starting production, and workover fluids, used in remedial operations usually on a well that is already producing.

During the operations for drilling and completing hydrocarbon-bearing formations (reservoirs), an overbalance pressure is often applied which causes fluid loss from the wellbore into the reservoir rock. This filtration process causes solid particles to block pores in the formation with the build-up of a low permeability internal filtercake comprised of the solid phases present in the fluid, as shown figure 1. The depth of invasion may be from a few millimetres to (occasionally) many centimeters. This is the primary cause of damage (loss of productivity) in open hole wells, a phenomenon which is increased by a large overbalance pressure. Furthermore the formation of a

thick filter cake may lead to an increased risk of getting drill pipes and measuring tools stuck in the wellbore and to failure in cementing the wellbore casings.

Mud solid invasion is also important when the well comprises large natural fractures as shown figure 2. The fractures invaded by the mud are no longer available to drain the oil into the wellbore. In workover operations, perforations may be also invaded in the same way.

It is therefore highly desirable to provide means to reduce these kinds of formation damage.

High fluid loss, especially spurt loss, tends to increase mud invasion. Accordingly, additives of a polymeric type, such as biopolymers (Xanthan, Scleroglucan), starches and celluloses (hydroxyethyl cellulose[HEC], polyanionic cellulose [PAC]), are added to provide viscosity and fluid loss control.

Usually wellbore fluids also contain inorganic solids such as clays, barite and calcium carbonate. When considering minimising mud invasion, an important aspect in selecting such inorganic solids is their particle size distribution for the particles to seal the entrance to pores or fractures in the reservoir rock. The "bridging" solids are combined with water soluble or colloidal polymers to enhance the seal.

Sized particles limit the depth of invasion as shown figures 3 and 4, where the pore or fracture entrance is sealed with bridging solids. The solids used include for instance ground silica (especially common in fracturing operations), mica, calcium carbonate, ground salts and oil soluble resins.

Another often interrelated approach is to use soluble solids to allow subsequent clean-up with wash fluids. Accordingly sized calcium carbonate (that can be dissolved by acid and therefore be removed from the pores) is a typical component of drill-in fluids. The polymers used in conjunction with the calcium carbonate are often selected on the basis that they can also be broken down by acid or enzyme treatments to prevent them impairing the permeability of the formation.

However, these remedial treatments involving the use of strong acid (for instance 15% HCl) have a high cost and can be hazardous and ineffective for the following reasons. Poor dissolution of the filter cake can be caused by zones of higher permeability channelling acid away and into the formation. This can lead to further formation damage. Strong acids involve health and safety

issues and cause corrosion of sand screens and downhole equipment. Treating a wellbore interval also raises placement issues. Moreover, laboratory tests have shown that the acids can be damaging to the reservoir rock matrix.

Because of these limitations there are many systems and products on the market to try and improve the performance of filter cake clean up treatments. However, these tend to have associated problems. For example, the use of alkaline oxidising agents can lead to problems of iron oxide scale in metal tubulars. Enzymes take a long time to react and are limited in application by temperature, pH and salinity. Internal breakers, such as magnesium peroxide, can be added to the reservoir drill-in fluid so it forms part of the filter cake. This is then activated by acid to produce hydrogen peroxide to facilitate the breakdown the polymers in the cake. Unfortunately, this can actually happen in the reservoir drill in fluid whilst drilling which can have a negative effect on fluid properties.

The present invention aims at providing new wellbore fluids which can form an easy-to-remove filter cake.

The invention provides a fluid system that, when used for the purposes of drilling, completing, cementing, stimulating, packing or working over a wellbore, will facilitate filter cake removal. This fluid system can comprise aqueous or non-aqueous based fluids (such as hydrocarbon based fluids). The result will be reduced or often negligible impairment of permeability of the producing formation by the relevant reservoir servicing fluid compared with well servicing fluids containing conventional bridging materials.

In accordance with the present invention, acetal crosslinked polymers are used as the bridging agent in the relevant fluid. In essence the bridging material is made of a particulate material which may swell but is substantially insoluble in water under non-acidic conditions (at $\text{pH} > 7.5$) and which is degraded at acidic pH (below 6.5) to substantially solids-free or soluble decomposition products. The particles are composed of the reaction product of A) one or more water soluble organic compound(s) having a molecular weight of less than 30,000 and possessing at least two hydroxyl groups and B) any other organic compound(s) capable of forming acetal or hemiacetal cross-links with the hydroxyl groups of compound A.

Examples of compounds A with free hydroxyl groups capable of entering into the crosslink reaction of the invention include monosaccharides, oligosaccharides, polysaccharides of molecular weight less than 30,000, glycerol, polyglycerols, erythritol, pentaerythritol, mannitol, sorbitol, glycols, polyalkylene glycols, and low molecular weight water soluble vinyl polymers possessing hydroxyl groups.

Suitable acetal crosslink agents B include aliphatic monoaldehydes and dialdehydes having from 2 to 10 carbon atoms and esters of propiolic acid wherein the alcohol forming the ester has from 1 to 8 carbons. A preferred compound is 1,5 pentanedial (glutaric dialdehyde) $C_5H_8O_2$.

Usually, the amount of cross-linking agent varies from 0.5 to 15% w/w (and the amount of compound A accordingly varies from 99.5 to 85% w/w).

An example of a useful material has been prepared from 95% yellow dextrin (a gum produced from the acid hydrolysis and depolymerisation of starch feedstock) and 5% by weight pentanedial.

Acetal crosslinked starches are known from U.S. Patents 4,048,435 and 4,098,997 that describe methods of preparing reversibly crosslinked granular starches for use in the paper, adhesives and textile industries but with no mention as to their potential use in the oil industry. It is stated that these starches contain acetal crosslinkages, which are stable under neutral or alkaline conditions but which readily hydrolyse under acidic conditions, and they are designed to dissolve and form a colloidal suspension in water. By contrast, the present invention contemplates the cross-linking of much lower molecular weight polyols than the above mentioned starches to produce a particulate suspension where the particles do not dissolve or disperse at alkaline pH.

The solid may be ground or prepared to any desired particle size.

The particles are stable under alkaline conditions and insoluble (but usually swell) in aqueous wellbore fluids of pH 7.5 and above. Thus they provide very effective sealing of the formation by virtue of the swollen particles' ability to deform to "fit" the pore openings or fractures.

Most advantageously however, the cross links rapidly hydrolyse under acidic catalysed conditions, under even weakly acidic conditions at pH 6.5 and below. The degradation products are essentially solids free water soluble moieties of low molecular weight and low viscosity in solution. Hence any flow restriction (of hydrocarbons) caused by the particles may be efficiently

removed. A low pH solution such as a weak easily-handled acid of little corrosion potential may be pumped in place to catalytically degrade the particles. Alternatively, produced fluids, be they oil and water or gas and water, usually exhibit an aqueous pH of less than pH 6.5 due to the carbon dioxide commonly present. Hence the removal of the temporary seal may be triggered simply by allowing the well to flow. As the seal degrades the well flow increases autocatalytically.

The hydrolysis does not consume the acid. Hence much enhanced clean up and optimised well productivity is anticipated compared to that exhibited when using current materials such as ground calcium carbonate.

The following features and benefits have been identified with the use of acetal crosslinked, polymeric, bridging solids:

- Filter cakes made from these novel materials almost totally degrade in the presence of weak acid giving almost 4x the return flow rate compared to a corresponding calcium carbonate based fluid under the same conditions. This also gives the benefits of better health and security from handling weak acids and less corrosion of downhole screens and equipment.
- A feature of the invention is that the degradation of the acetal bridging material is acid catalysed, as opposed to the conventional stoichiometric reaction. This means the acid is not consumed or neutralised in the reaction. The benefit of this is an enhanced acid treatment as the acid is available to go on degrading more filter cake.
- Due to the high mobility of the hydrogen ion (which can therefore penetrate the water-swollen particles), the acid does not have to be forced into the filter cake to break it down. Which means that less acid induced damage results from strong acid being forced into the formation causing fines to migrate, bridge and restrict production.
- Acetal crosslinked bridging materials can degrade under simulated well flowing conditions in the laboratory, where the weak acid is provided by produced CO₂ forming carbonic acid in the aqueous phase. This could negate the need for a costly wash fluid treatment.
- Acetal bridging materials have a low density. A low density will enable a wider range of applications to be covered, since density constraints often limit the amount of bridging solid which can be used. Calcium carbonate has a density of 2.7 S.G. and cannot always be added at

the desired concentration for bridging in low density fluids. Another benefit will be improved removal of undesirable, non acidisable, contaminating solids, from the fluid. Contaminating solids from the formation have roughly the same density as calcium carbonate which makes separation difficult in a conventional fluid. However, these solids are approximately 2.7 times denser than the acetal bridging solid. This means that highly efficient separation techniques, such as centrifugation, can be employed to remove non acidisable solids from the fluid without removing the acetal bridging solids. This therefore makes the fluid less formation damaging.

Preparation of an acetal bridging solid.

95 weight parts of dry yellow dextrin was dissolved in water and 5 weight parts pentanediol added. The sample was mixed and heated to 130°C. The water was then removed under partial vacuum over a 16 hour period. The solid from this was then ground to a fine particle size (substantially all less than 150 microns) and tested as follows.

The wellbore fluids in the following examples have been tested using a high pressure/high temperature fluid loss cell as schematically represented figure 5. Such an apparatus typically comprises a measuring cell 1 closed by an upper cover provided with a central passage 2 and a bottom provided with a drain 3. The bottom is covered with a base made of a porous material, in this instance a 5 micron aloxite disc. Gas can be injected to provide the differential pressure between the mud and the formation fluids. The product doses are expressed in pounds per barrel (ppb).

Example 1

A fluid system of this invention (Acetal fluid) was compared to one of conventional formulation, CaCO_3 based fluid (comparison fluid) containing 49ppb calcium carbonate bridging solids, 6ppb DUALFLO filtration control additive, 1ppb IDVIS viscosifier and suspending agent, 25ppb CaCl_2 , 2ppb PTS200 alkaline buffer.

The Acetal fluid contains 40ppb ACETAL bridging solids, 6ppb DUALFLO, 1ppb IDVIS, 43ppb KCl, 2ppb PTS200.

The testing of the fluids was according to the following protocol, schematically illustrated figure 5 where the arrows indicate the direction of the fluid flow in the core plugs (the upwards arrow corresponds to fluid loss from the subterranean rock to the wellbore while the downwards arrow characterises fluid loss from the wellbore into the subterranean rock).

- Step 1: 'apply' mud damage, using the tested wellbore fluid, to a 5 micron aloxite disc under typical well conditions (temperature 80° C, pressure of 500 psi). Fluid loss is measured after 15.5 hours (downwards arrow). A filter cake is formed on the aloxite disc.
- Step 2: cell emptied hot and refilled with 10% NaCl brine and 12/20 sand. A 45 micron aperture screen was then placed on the sand. The sand is used for modelling a gravel pack which may be placed in a well to control sand production.
- Step 3: simulates the flow from the reservoir oil into the wellbore through the filter cake (upwards arrow) , using kerosene flow back and a typical formation pressure of 4 psi with carbon dioxide as the pressuring gas at 80°C.
- Step 4 : Flow 500g of CO₂ containing kerosene, shut the cell and leave for 64 hours at 80°C and then test the flow rate in the production direction

Sample	15.5 hr. Fluid loss	Flow rate after shut in
	(ml)	(g/min)
CaCO ₃ bridging solids	17	22..2
Acetal bridging solids	20	33.6

The example illustrates the effect that an ACETAL fluid filter cake is degraded in the presence kerosene containing dissolved carbon dioxide. The return flow rate for the ACETAL fluid was 1.5 x higher than for the CaCO₃ fluid. This test suggests that naturally occurring fluids from a production zone will degrade the filter cake even in the absence of applied acid. It can also be seen

that using all acetal based solids gives a slightly higher fluid loss. It was found that the use of a small amount of calcium carbonate in conjunction with the acetal solids reduced the filtrate loss, allowing a lower concentration of DUALFLO fluid loss additive to be utilised in the following examples.

Example 2

The CaCO_3 based fluid contains - 40ppb calcium carbonate, 6ppb DUALFLO, 1ppb IDVIS, 43ppb KCl, 1ppb PTS100.

The ACETAL based fluid contains - 7ppb calcium carbonate, 30ppb ACETAL solids, 3ppb DUALFLO, 1ppb IDVIS, 43ppb KCl, 3ppb PTS100.

The following test protocol is used

- Step 1: 'apply' mud damage, using the tested wellbore fluid, through a 5 micron aloxite disc at a temperature of 80° C and a pressure of 500 psi. The fluid loss is measured after 15.5 hours.
- Step 2: cell emptied hot and refilled with 100 ml 5% citric acid as a moderated acidic wash fluid.
- Step 3: Reseal cell, do not pressurise, leave 72 hours at 80°C
- Step 4 : Open cell and fill with 12-20 sand and fit 45 micron aperture screen
- Step 5: Carry out kerosene return flows at 4psi, at a temperature of 80°C.

Sample	16.5 hr. Fluid loss (ml)	Flow rate (g/min)	pH of produced fluids
CaCO_3 fluid	23	21.2	5.9
ACETAL fluid	17	80.9	2.0

The example signifies that under mild acid conditions the return flow rate for the ACETAL fluid was nearly 4x higher than for the CaCO_3 fluid, indicating that the ACETAL fluid filter cake has degraded to a much greater extent. This was confirmed on opening the cell which showed the presence of a large filter cake for the CaCO_3 fluid and little to no filter cake for the ACETAL fluid. The lower pH of the produced fluids from the cell containing the ACETAL filter cake indicates that the acid is not being used up to the same extent as with CaCO_3 filter cake. The example also demonstrates that the filter cake is degraded without pressurisation of the cell. Conventionally, these tests are typically carried out under pressure to force acid into the cake.

Example 3

The CaCO_3 based fluid contains - 40ppb calcium carbonate, 6ppb DUALFLO, 1ppb IDVIS, 43ppb KCl, 2ppb PTS200, 15ppb OCMA clay.

The ACETAL based fluid contains - 7ppb calcium carbonate, 30ppb ACETAL solids, 3ppb DUALFLO, 1ppb IDVIS, 43ppb KCl, 3ppb PTS100 15ppb OCMA clay.

The test protocol of example 2 was used except that step 1 lasted only 15.5 hours and step 3 20hours.

Sample	15.5 hr. Fluid loss	Flow rate
	(ml)	(g/min)
CaCO_3 fluid	32	9.8
ACETAL fluid	18.8	21.4

The example demonstrates that an ACETAL fluid filter cake containing non acidisable OCMA clay is degraded by weak acid in a short time. The return flow rate for the ACETAL fluid was 2.2

x higher than for the CaCO_3 fluid, indicating that the ACETAL fluid filter cake has degraded to a much greater extent.

Example 4

The CaCO_3 based fluid contains - 40ppb calcium carbonate, 6ppb DUALFLO, 1ppb IDVIS, 43ppb KCl, 2ppb PTS200.

The ACETAL based fluid contains - 10ppb calcium carbonate, 30ppb ACETAL solids, 3ppb DUALFLO, 1ppb IDVIS, 43ppb KCl, 2ppb PTS200.

The following test protocol was used :

- Step 1: 'apply' mud damage, using the tested wellbore fluid, through a 5 micron aloxite disc at a temperature of 80°C and a pressure of 500 psi. The fluid loss is measured after 15.5 hours.
- Step 2: cell emptied hot and refilled with 0.1m (0.37%w/v) HCl and 12/20 sand and a 45 micron aperture screen fitted.
- Step 3: The cell was resealed and left for 4hours @ 80°C
- Step 4: then kerosene flow backs carried out at 4psi and 80°C .

Sample	15.5 hr. Fluid loss (ml)	Flow rate (g/min)
CaCO_3 fluid	29	20.7
ACETAL fluid	16	32.0

The example demonstrates that exposure of ACETAL fluid filter cake to even a highly diluted acid causes it to degrade in only a short time. The return flow rate for the ACETAL fluid was 1.5 x higher than for the CaCO_3 fluid.

Claims

1. A wellbore fluid comprising a particulate material composed of the reaction product of A) one or more water soluble organic compound(s) having a molecular weight of less than 30,000 and possessing at least two hydroxyl groups and B) any other organic compound(s) capable of forming acetal or hemiacetal cross-links with the hydroxyl groups of compound A.
2. The wellbore fluid of claim 1, wherein hydroxyl compound A is selected from the class including monosaccharides, oligosaccharides, polysaccharides of molecular weight less than 30,000, glycerol, polyglycerols, erythritol, pentaerythritol, mannitol, sorbitol, glycols, polyalkylene glycols, and low molecular weight water soluble vinyl polymers possessing hydroxyl groups.
3. The wellbore fluid of claim 1 or claim 2, wherein compound B is selected from the class including aliphatic aldehydes and dialdehydes having from 2 to 10 carbon atoms, and esters of propionic acid wherein the alcohol forming the ester has from 1 to 8 carbon atoms.
4. The wellbore fluid of any preceding claim, wherein 0.5-15% dry weight of compound A reacted with 99.5-85% of said compound B.
5. The wellbore fluid of any preceding claim, wherein the particulate material is the reaction product of dextrin and pentanediol.
6. Application of the wellbore fluid according to any of the preceding claim as any of the following well processes : drilling, under-reaming, completing, working over, sealing loss zones, sealing fractures, sealing cavities or other very high permeability conduits in a rock formation, or hydraulic fracturing to stimulate a hydrocarbon-producing zone
7. A process wherein after any of the well processes of claim 6, a low pH fluid containing any acid or buffered solution of less than pH 6.0 is pumped into the producing zone segment of the wellbore to catalyse the decomposition of the particulate material of this invention.
8. A process wherein, after any of the well processes in claim 6 or claim 7, the well is allowed to flow causing a drop in pH which catalyses the decomposition of the particulate solids of this invention permitting yet increased flow of produced fluids.

9. A particulate material composed of the reaction product of A) one or more water soluble organic compound(s) having a molecular weight of less than 30,000 and possessing at least two hydroxyl groups and B) any other organic compound(s) capable of forming acetal or hemiacetal cross-links with the hydroxyl groups of compound A.
10. The particulate material of claim 9, wherein the hydroxyl compound A is selected from the class including monosaccharides, oligosaccharides, polysaccharides of molecular weight less than 30,000, glycerol, polyglycerols, erythritol, pentaerythritol, mannitol, sorbitol, glycols, polyalkylene glycols, and low molecular weight water soluble vinyl polymers possessing hydroxyl groups.
11. The particulate material of claim 9, wherein the compound B is selected from the class including aliphatic aldehydes and dialdehydes having from 2 to 10 carbon atoms, and esters of propiolic acid wherein the alcohol forming the ester has from 1 to 8 carbon atoms.

Wellbore Fluid

The present invention relates to a wellbore fluid comprising a particulate material composed of the reaction product of A) one or more water soluble organic compound having possessing a molecular weight of less than 30,000 and possessing at least two hydroxyl groups and B) any other organic compound(s) capable of forming acetal or hemiacetal cross-links with the hydroxyl groups of compound A. The invention relates also to the specific particulate material itself and to applications of the wellbore fluid of the invention for well processes such as drilling, under-reaming, completing, working over, sealing loss zones, sealing fractures, sealing cavities or other very high permeability conduits in a rock formation, or hydraulic fracturing to stimulate a hydrocarbon-producing zone.

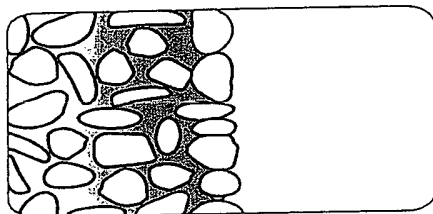


Figure 1

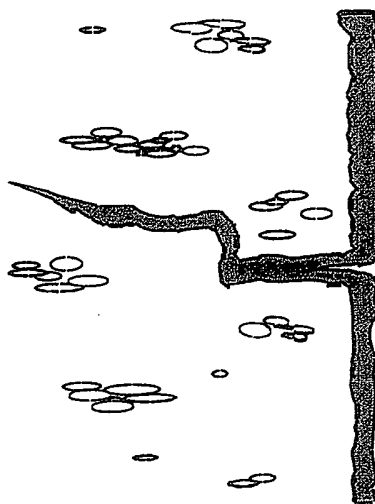


Figure 2

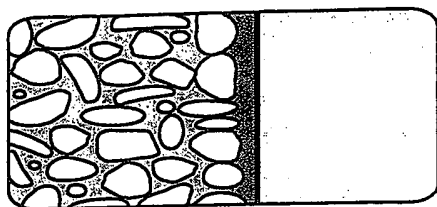


Figure 3



Figure 4

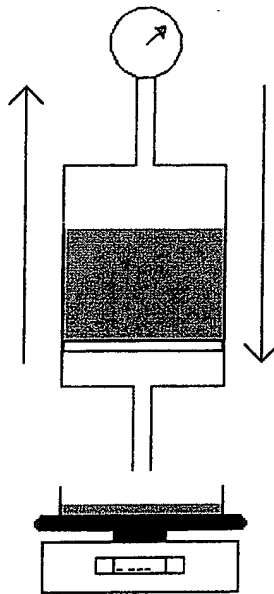


Figure 5

Claims

1. A wellbore fluid comprising a particulate material composed of the reaction product of A) one or more water soluble organic compound having possessing a molecular weight of less than 30,000 and possessing at least two hydroxyl groups and B) any other organic compound(s) capable of forming acetal or hemiacetal cross-links with the hydroxyl groups of compound A.
2. The wellbore fluid of claim 1 wherein hydroxyl compound (A) is selected from the class including monosaccharides, oligosaccharides, polysaccharides of molecular weight less than 30,000, glycerol, polyglycerols, erythritol, pentaerythritol, mannitol, sorbitol, glycols, polyalkylene glycols, and low molecular weight water soluble vinyl polymers possessing hydroxyl groups.
3. The wellbore fluid according to claim 1 or 2, wherein compound (B) is selected from the class including aliphatic aldehydes and dialdehydes having from 2 to 10 carbon atoms, and esters of propionic acid wherein the alcohol forming the ester has from 1 to 8 carbon atoms.
4. The wellbore fluid according to any of the preceding claim, wherein 0.5-15%, dry weight of compound (A) and 95.5-85% of said compound (B) is reacted.
5. The wellbore fluid according to any of the preceding claim wherein the particulate material is the reaction product of dextrin and pentanedial.
6. Application of the wellbore fluid according to any of the preceding claim as any of the following well processes : drilling, under-reaming, completing, working over, sealing loss zones, sealing fractures, sealing cavities or other very high permeability conduits in a rock formation, or hydraulic fracturing to stimulate a hydrocarbon-producing zone
7. A process wherein after any of the well processes of claim 6, a low pH fluid containing any acid or buffered solution of less than pH 6.0 is pumped into the producing zone segment of the wellbore to catalyse the decomposition of the particulate material of this invention.
8. A process wherein, after any of the well processes in Claims 6 or 7, the well is allowed to flow causing a drop in pH which catalyses the decomposition of the particulate solids of this invention permitting yet increased flow of produced fluids.

9. A particulate material composed of the reaction product of A) one or more water soluble organic compound having possessing a molecular weight of less than 30,000 and possessing at least two hydroxyl groups and B) any other organic compound(s) capable of forming acetal or hemiacetal cross-links with the hydroxyl groups of compound A.
- 5 10. The particulate material of claim 9, wherein the hydroxyl compound (A) is selected from the class including monosaccharides, oligosaccharides, polysaccharides of molecular weight less than 30,000, glycerol, polyglycerols, erythritol, pentaerythritol, mannitol, sorbitol, glycols, polyalkylene glycols, and low molecular weight water soluble vinyl polymers possessing hydroxyl groups.
- 10 11. The particulate material as in Claim 9 wherein the compound (B) is selected from the class including aliphatic aldehydes and dialdehydes having from 2 to 10 carbon atoms, and esters of propionic acid wherein the alcohol forming the ester has from 1 to 8 carbon atoms.

Claims

1. A wellbore fluid comprising a water-non soluble particulate material composed of the reaction product of A) one or more water soluble organic compound having possessing a molecular weight of less than 30,000 and possessing at least two hydroxyl groups and B) any other organic compound(s) capable of forming acetal or hemiacetal cross-links with the hydroxyl groups of compound A.
2. The wellbore fluid of claim 1 wherein hydroxyl compound (A) is selected from the class including monosaccharides, oligosaccharides, polysaccharides of molecular weight less than 30,000, glycerol, polyglycerols, erythritol, pentaerythritol, mannitol, sorbitol, glycols, polyalkylene glycols, and low molecular weight water soluble vinyl polymers possessing hydroxyl groups.
3. The wellbore fluid according to claim 1 or 2, wherein compound (B) is selected from the class including aliphatic aldehydes and dialdehydes having from 2 to 10 carbon atoms, and esters of propiolic acid wherein the alcohol forming the ester has from 1 to 8 carbon atoms.
4. The wellbore fluid according to any of the preceding claim, wherein 0.5-15%, dry weight of compound (A) and 95.5-85% of said compound (B) is reacted.
5. The wellbore fluid according to any of the preceding claim wherein the particulate material is the reaction product of dextrin and pentanediol.
6. Application of the wellbore fluid according to any of the preceding claim as any of the following well processes : drilling, under-reaming, completing, working over, sealing loss zones, sealing fractures, sealing cavities or other very high permeability conduits in a rock formation, or hydraulic fracturing to stimulate a hydrocarbon-producing zone
7. A process wherein after any of the well processes of claim 6, a low pH fluid containing any acid or buffered solution of less than pH 6.0 is pumped into the producing zone segment of the wellbore to catalyse the decomposition of the particulate material of this invention.

8. A process wherein, after any of the well processes in Claims 6 or 7, the well is allowed to flow causing a drop in pH which catalyses the decomposition of the particulate solids of this invention permitting yet increased flow of produced fluids.